Chapter 5

Molecular Magnetic Properties

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Introduction

The following notes represent an attempt to bring together into a coherent whole arguments from electrodynamics and quantum mechanics that may be useful to an understanding of response properties of a molecule in the presence of two magnetic perturbations, namely a spatially uniform, time-independent external field and an intramolecular permanent dipole moment placed on a nucleus.

The first section is aimed at showing how far one can go using the tools of classical physics, its contradictions and failure to explain paramagnetism, and the need for quantum mechanical theories, which only can be used to rationalize magnetic susceptibilities and nuclear magnetic shieldings in molecules.

Section II deals with the definition of quantum mechanical current density, induced by magnetic perturbations within the electron cloud, and its properties. The hydrodynamical foundation of quantum mechanics is reviewed, introducing the concept of Madelung-London-Landau local mean velocity and deducing its equation of motion, formally identical to Newton equation. A "vorticity condition" for the quantum mechanical current density is obtained as a consequence of quantization constraint.

[1] L.A. Montero, L.A. Díaz and R. Bader (eds.), Introduction to Advanced Topics of Computational Chemistry, 105 - 136, 2003,

The sum rules for gauge invariance of theoretical magnetic properties, and their connection with relationships for charge and current conservation are examined in the light of the fundamental Nöther theorem.

Special methods for computing magnetic properties within the framework of a continuous transformation of the origin of the current density are presented in Section III. The invariance to a gauge translation of magnetic properties calculated via such procedures within the algebraic approximation is discussed.

The level of discussion, both as regards mathematics and physics, is elementary to make the text readily accessible to undergraduate students.

5.1 CLASSICAL CURRENT DENSITY INDUCED BY A STATIC MAGNETIC FIELD

5.1.1 The Larmor precession

Let us consider the finite motion of a system of n classical (spinless) particles with mass m_i and charge q_i. With respect to an inertial frame K, that is, the space set of axes in the laboratory, the particles have position coordinates $\mathbf{r}_i$, velocities $\mathbf{v}_i$ and linear momenta $\mathbf{p}_i = m_i\mathbf{v}_i$. The angular momentum and the magnetic dipole moment of the system of particles with respect to the origin are respectively

$$\mathbf{L} = \sum_{i=1}^{n} \mathbf{l}_i, \qquad \mathbf{l}_i = \mathbf{r}_i \times \mathbf{p}_i, \tag{1.1}$$

$$\mathbf{m} = \frac{1}{2c} \sum_{i=1}^{n} \frac{q_i}{m_i} \mathbf{l}_i. \tag{1.2}$$

When the particles have a uniform $\frac{q}{m}$ ratio, the magnetogyric ratio is defined [1]

$$\Gamma = \frac{q}{2mc}, \tag{1.3}$$

so that

$$\mathbf{m} = \Gamma \mathbf{L}. \tag{1.4}$$

Vectors $\mathbf{L}$ and $\mathbf{m}$ are origin–independent if the total linear momentum vanishes,

$$\mathbf{P} = \sum_{i}^{n} \mathbf{p}_i = \mathbf{0},$$

that is, if the center of mass of the particle distribution is at rest in K.

We will be interested in the stationary motion of the particle distribution. In this case it is convenient to introduce the time–average of a dynamical variable f,

$$\overline{f} = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau f(t)dt.$$

In the presence of a time–independent spatially uniform magnetic field with induction $\mathbf{B}$ the energy of the average magnetic dipole is

$$W = -\overline{\mathbf{m}} \cdot \mathbf{B}. \tag{1.5}$$

The magnetic field also exerts an average torque on the magnetic dipole,

$$\overline{\mathbf{K}} = \overline{\mathbf{m}} \times \mathbf{B}, \tag{1.6}$$

so that, from eqs. (1.3), (1.4) and (1.6), the equation of motion for the total average angular momentum is

$$\frac{d\overline{\mathbf{L}}}{dt} = \overline{\mathbf{K}} = -\Gamma\mathbf{B} \times \overline{\mathbf{L}}. \tag{I.7}$$

For any vector $\mathbf{V}$ of constant magnitude, rotating counterclockwise in space about an axis $\mathbf{n}$ fixed in K, with angular velocity Ω, the time rate of change is

$$\frac{d\mathbf{V}}{dt} = \Omega \times \mathbf{V}. \tag{1.8}$$

Hence, owing to eqs. (1.7) and (1.8), the magnetic field induces a uniform precession of $\overline{\mathbf{L}}$ (and $\overline{\mathbf{m}}$) about the direction of $\mathbf{B}$ with angular velocity

$$\Omega_L = -\Gamma\mathbf{B}. \tag{1.9}$$

The modulus Ω_L is known as Larmor frequency [1]. For electrons $q = -e$, Γ is negative, and the Larmor precession is counterclockwise.

5.1.2 Larmor's theorem

Let us consider a classical (spinless) particle of mass m, charge q and position $\mathbf{r}_s = \mathbf{r}_s(t)$, moving with velocity $\mathbf{v}_s$ with respect to K_s, the inertial system fixed in the laboratory, in the central electric field $\mathbf{E}$ of another particle Q in the origin of K_s, and in the presence of the spatially uniform time–independent magnetic field $\mathbf{B}$. For an observer in K_s, the Lorentz force acting on the particle is

$$\mathbf{F}_s = q\mathbf{E} + \frac{q}{c}\mathbf{v}_s \times \mathbf{B}, \tag{1.10}$$

and the equation of motion is

$$\mathbf{F}_s = m\mathbf{a}_s = m\left(\frac{d\mathbf{v}_s}{dt}\right)_s. \tag{1.11}$$

Let us introduce a coordinate system K_r rotating with the Larmor angular velocity

$$\Omega_L = -\frac{q}{2mc}\mathbf{B}.$$

We assume K_s and K_r axes as instantaneously coincident at time t, so that

$$\mathbf{r}_s = \mathbf{r}_r \equiv \mathbf{r}.$$

The time rate of change of any vector, is given by the operator equation [1,2]

$$\left(\frac{d}{dt}\right)_s = \left(\frac{d}{dt}\right)_r + \Omega_L \times, \tag{1.12}$$

thus, for a given vector $\mathbf{A}_s$ defined in K_s,

$$\left(\frac{d\mathbf{A}_s}{dt}\right)_s = \left(\frac{d\mathbf{A}_s}{dt}\right)_r + \Omega_L \times \mathbf{A}_s. \tag{1.12'}$$

For $\mathbf{A}_s \equiv \mathbf{r}$, eq. (1.12′) relates the velocity of the particle in the stationary system to that in the rotating system,

$$\mathbf{v}_s = \mathbf{v}_r + \Omega_L \times \mathbf{r}, \tag{1.13}$$

and, for $\mathbf{A}_s \equiv \mathbf{v}_s$, the analogous equation for the accelerations in K_s and K_r is

$$\mathbf{a}_s = \mathbf{a}_r + 2\Omega_L \times \mathbf{v}_r + \Omega_L \times (\Omega_L \times \mathbf{r}). \tag{1.14}$$

¿From this result we find the effective force $\mathbf{F}_r$ acting in the rotating system; it contains Coriolis and centrifugal terms [3]

$$\mathbf{F}_r = \mathbf{F}_s + 2m\mathbf{v}_r \times \Omega_L + m(\Omega_L \times \mathbf{r}) \times \Omega_L. \tag{1.15}$$

¿From eqs.(1.9)–(1.11) and (1.13)–(1.15), the equation of motion in the rotating system has the simple form

$$\mathbf{F}_r = m\mathbf{a}_r = q\mathbf{E} + m\Omega_L \times (\Omega_L \times \mathbf{r}), \tag{1.16}$$

from which the term linear in $\mathbf{B}$ has disappeared. If the last term is neglected, eq. (1.16) becomes the equation of motion of the particle in a central electric field, referred to the rotating system. The effective magnetic field $\mathbf{B}_r$, acting on the particle in K_r, is identically vanishing.

This result can be generalized to discuss the precession of the angular momentum of a single particle with respect to a system rotating with angular velocity Ω, in the presence of the magnetic field $\mathbf{B}$, using the following argument [2]. The instantaneous angular momentum of the particle is [3]

$$\mathbf{l}_s = \mathbf{l}_r \equiv \mathbf{l},$$

but, from (1.12), and using the equation of motion for $\mathbf{l}$ analogous to (1.7), one has

$$\left(\frac{d\mathbf{l}}{dt}\right)_r = \left(\frac{d\mathbf{l}}{dt}\right)_s - \Omega \times \mathbf{l} = \mathbf{l} \times (\Omega - \Omega_L) = \Gamma \mathbf{l} \times \mathbf{B}_r, \tag{1.17}$$

where

$$\mathbf{B}_r = \mathbf{B} + \frac{1}{\Gamma}\Omega \tag{1.18}$$

is the effective magnetic field acting upon the particle in a coordinate system rotating with angular velocity Ω. When $\Omega = \Omega_L$, $\mathbf{B}_r = \mathbf{0}$, and $\mathbf{l}$ is stationary in K_r.

These findings constitute the Larmor theorem [4]: for a fixed observer, to first order in $\mathbf{B}$, the effect of the magnetic field on a charge q is that of inducing a precession with angular velocity $\Omega_L = -\Gamma\mathbf{B}$, superimposing to its normal motion. Thus a fixed system K_s in an external magnetic field $\mathbf{B}$ is equivalent to a reference system K_r without magnetic field, rotating with angular velocity

$$\Omega = \frac{q}{2mc}\mathbf{B} = -\Omega_L,$$

so that, also for an observer in K_r, the charge q precesses with angular velocity Ω_L. One can alternatively say that in a coordinate frame K_r, rotating with angular velocity Ω, there is an apparent magnetic field

$$\mathbf{B} = \frac{2mc}{q}\Omega$$

acting on charge q.

On the one hand, the (adiabatic) switching on of the magnetic field $\mathbf{B}$ can be thought of as an *active* transformation, leaving the coordinate system K_s fixed, and inducing a rigid rotation of the physical space, i.e., a precession of charges with angular velocity $\Omega_L = -\Gamma\mathbf{B}$. On the other hand, the choice of the alternative coordinate system K_r, rotating with angular velocity $\Gamma\mathbf{B} = -\Omega_L$, amounts to a backward *passive* transformation, leaving the charge distribution fixed. Although conceptually different, these transformations are equivalent in practice.

We emphasize that neglecting the centrifugal contribution in eq. (1.16), a term to second order in $\mathbf{B}$, does not lead to any major problem. Let us consider, for instance, the Larmor precession of an electron in the first Bohr orbit of hydrogen atom. Indicating with a_0 the Bohr radius and with e the proton charge, the radial electric force is

$$F_r = -\frac{e^2}{a_0^2},$$

that is, $\approx 8.24 \times 10^{-3}$ dyne. In a magnetic field of 10^5 Gauss, i.e., 10 Tesla, using tabulated values [5], the linear term in $\mathbf{B}$ is $\approx 3.51 \times 10^{-7}$ dyne, and the centrifugal term quadratic in $\mathbf{B}$, $\approx 3.73 \times 10^{-12}$ dyne, can be safely neglected.

5.1.3 Classical current density, magnetic susceptibility and nuclear magnetic shielding

The statements we have made so far for discrete charges q_i can be extended to a continuous distribution of charge density $\rho(\mathbf{r}) = q\gamma(\mathbf{r})$ via the formal replacement

$$\sum_{i=1}^{n} q_i \rightarrow \int dV \rho(\mathbf{r}).$$

For a point charge at $\mathbf{r}_0$, $\rho(\mathbf{r}) \equiv q\delta(\mathbf{r} - \mathbf{r}_0)$. For instance, the expression for the magnetic dipole becomes

$$\mathbf{m} = \frac{1}{2c} \int dV \rho(\mathbf{r}) \mathbf{r} \times \mathbf{v}. \tag{1.2$'$}$$

Let us consider a system of charges confined within the volume V. S is the closed surface enclosing the integration volume V, and the vector $d\mathbf{S} = \mathbf{n}dS$ is directed along the external line perpendicular to the surface S. The time rate of change of total charge in the volume V is [4]

$$\frac{\partial}{\partial t} \int_V \rho(\mathbf{r}) dV = - \int_S \rho(\mathbf{r}) \mathbf{v} \cdot d\mathbf{S} = - \int_V \nabla \cdot \mathbf{J}(\mathbf{r}) dV \tag{1.19}$$

where $\rho \mathbf{v} \cdot d\mathbf{S}$ is the charge crossing the surface element $d\mathbf{S}$ with velocity $\mathbf{v}$. The last identity arises from the Gauss divergence theorem, where we have used

$$\mathbf{J} = \rho \mathbf{v}, \tag{1.20}$$

Eq. (1.19) is called continuity equation in integral form. As it holds for any V, the differential condition

$$\nabla \cdot \mathbf{J} + \frac{\partial}{\partial t} \rho = 0 \tag{1.21}$$

is to be satisfied. In terms of $\gamma = \frac{1}{q}\rho$ and $\mathbf{j} = \frac{1}{q}\mathbf{J}$,

$$\nabla \cdot \mathbf{j} + \frac{\partial}{\partial t} \gamma = 0. \tag{1.22}$$

Some formulae can be rewritten using the expression for the current density, for instance,

$$\mathbf{m} = \frac{1}{2c} \int dV \mathbf{r} \times \mathbf{J} \tag{1.2$''$}$$

is the permanent (unperturbed) magnetic moment of a charge distribution, compare for eq. (1.2$'$). Its energy in the magnetic field is

$$W = -\mathbf{m} \cdot \mathbf{B} = -\frac{1}{c} \int dV \mathbf{A} \cdot \mathbf{J}. \tag{1.5$'$}$$

For a charge distribution precessing in a central electric field $\mathbf{E}$, e.g., in the case of a diamagnetic atom, it is expedient to define a Larmor current density $\mathbf{J}_L(\mathbf{r})$. From the

general formula (1.20) and eq. (1.13), the contribution provided by the Larmor precession is

$$\mathbf{J}_L = \rho\Omega_L \times \mathbf{r} = -\frac{q}{mc}\rho\mathbf{A}. \tag{1.23}$$

In eqs. (1.5') and (1.23)

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r} \tag{1.24}$$

is the vector potential with respect to the origin. Eq. (1.23) has been obtained via the formal replacement

$$\mathbf{v} \to \mathbf{v}' = \mathbf{v} - \frac{q}{mc}\mathbf{A}, \tag{1.25}$$

i.e., the contribution to the radial velocity of an element of charge due to the Larmor precession is

$$\mathbf{v}_L = \frac{\mathbf{J}_L}{\rho} = -\frac{q}{mc}\mathbf{A}, \tag{1.26}$$

satisfying the general equation

$$\Omega_L = \frac{1}{2}\nabla \times \mathbf{v}_L. \tag{1.27}$$

For electron densities, $\mathbf{J}_L$ is clockwise around the direction of $\mathbf{B}$. The trajectories lie in planes perpendicular to the inducing magnetic field.

The magnetic field induced via a feedback effect at point $\mathbf{r}_0$ by the perturbed charge distribution is given by the Biot–Savart law,

$$\mathbf{B}_L(\mathbf{r}_0) = \frac{1}{c}\int \frac{\mathbf{r}-\mathbf{r}_0}{|\mathbf{r}-\mathbf{r}_0|^3} \times \mathbf{J}_L(\mathbf{r})dV = -\sigma_L(\mathbf{r}_0)\cdot\mathbf{B}, \tag{1.28}$$

where $\mathbf{r}$ is the distance of the volume element dV from the origin, so that the effective field acting on the point $\mathbf{r}_0$ is $\mathbf{B} + \mathbf{B}_L(\mathbf{r}_0)$. The tensor

$$\sigma_L(\mathbf{r}_0) = \frac{q^2}{2mc^2}\int dV\gamma(\mathbf{r})\left[\mathbf{r}\cdot\frac{(\mathbf{r}-\mathbf{r}_0)}{|\mathbf{r}-\mathbf{r}_0|^3}\mathbf{1} - \mathbf{r}\frac{(\mathbf{r}-\mathbf{r}_0)}{|\mathbf{r}-\mathbf{r}_0|^3}\right], \tag{1.29}$$

describes the magnetic shielding at point $\mathbf{r}_0$, arising from the Larmor precession.

The first–order magnetic moment due to the Larmor precession,

$$\mathbf{m}_L = \frac{1}{2c}\int dV\mathbf{r} \times \mathbf{J}_L = \chi_L \cdot \mathbf{B}, \tag{1.30}$$

and its second–order interaction energy with the magnetic field

$$W_L = -\frac{1}{2c}\int dV\mathbf{A}\cdot\mathbf{J}_L = -\frac{1}{2}\mathbf{m}_L\cdot\mathbf{B} = -\frac{1}{2}\mathbf{B}\cdot\chi_L\cdot\mathbf{B}, \tag{1.31}$$

are written in terms of

$$\chi_L = -\frac{q^2}{4mc^2}\int dV\gamma(\mathbf{r})(r^2\mathbf{1} - \mathbf{rr}), \tag{1.32}$$

the magnetic susceptibility tensor of the charge distribution.

In the case of n electrons precessing around the nucleus of a diamagnetic atom, by taking the average over the directions of $\mathbf{r}$ within the integral in eq. (1.28), the average magnetic field induced on the nucleus at the origin of the coordinate system is

$$B_L(\mathbf{0}) = -\sigma_L^{Av}(\mathbf{0})B = \frac{e}{3mc^2}\phi_e(\mathbf{0})B, \tag{1.33}$$

where

$$\sigma_L^{Av}(\mathbf{0}) = \frac{1}{3}\mathrm{Tr}\sigma_L(\mathbf{0}) = \frac{e^2}{3mc^2}\sum_{i=1}^{n}\left(\frac{1}{r_i}\right)^{Av} \tag{1.34}$$

is the average magnetic shielding at the nucleus,

$$\phi_e(\mathbf{0}) = -e\int dV\gamma(\mathbf{r})\frac{1}{r} \tag{1.35}$$

is the (scalar) electric potential at the nucleus due to the electron cloud, and the average inverse distance of electrons from the origin is

$$\int dV\gamma(\mathbf{r})\frac{1}{r} = \sum_{i=1}^{n}\left(\frac{1}{r_i}\right)^{Av}.$$

Taking the average over $\mathbf{r}$ in (1.2″), the average magnetic dipole induced by the field is $m_L = \chi_L^{Av}B$, where

$$\chi_L^{Av} = \frac{1}{3}\mathrm{Tr}\chi_L = -\frac{e^2}{6mc^2}\sum_{i=1}^{n}\left(r_i^2\right)^{Av} \tag{1.36}$$

is the average magnetic susceptibility and

$$\int dV\gamma(\mathbf{r})r^2 \equiv \sum_{i=1}^{n}\left(r_i^2\right)^{Av}$$

is the average square distance of electrons from the origin.

Eq. (1.36) is known as Langevin formula (in the correct form given by Pauli [6]). χ_L^{Av} is called *diamagnetic* susceptibility, as the induced magnetic moment, according to Lentz's law, is antiparallel to the magnetic field.

It is expedient to introduce the perturbation expansion for the current density via the Taylor series

$$J_\alpha(\mathbf{r}) = J_\alpha^{(0)}(\mathbf{r}) + \mathcal{J}_\alpha^{B_\beta}(\mathbf{r})B_\beta + \ldots \tag{1.37}$$

The Larmor current density can be therefore written in terms of a first–order current density tensor of rank 2

$$J_{L\alpha} = \mathcal{J}_{L\alpha}^{B_\beta}B_\beta. \tag{1.38}$$

The magnetic susceptibility and the nuclear magnetic shielding at nucleus I, with position $\mathbf{R}_I$, can be rewritten (sum over repeated indices), compare with eqs. (1.32) and (1.29),

$$\chi_{L\alpha\delta} = \frac{1}{2c}\epsilon_{\alpha\beta\gamma}\int dV\, r_\beta\mathcal{J}_{L\gamma}^{B_\delta}(\mathbf{r}), \tag{1.39}$$

$$\sigma_{L\alpha\delta}^{I} = -\frac{1}{c}\epsilon_{\alpha\beta\gamma}\int dV\,\frac{r_\beta - R_{I\beta}}{|\mathbf{r}-\mathbf{R}_I|^3}\mathcal{J}_{L\gamma}^{B_\delta}(\mathbf{r}). \tag{1.40}$$

5.1.4 Charge conservation and gauge invariance

It is well known that the origin of the vector potential $\mathbf{A}$ can be chosen *ad libitum* [4], as the magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$ is invariant under a gauge transformation

$$\mathbf{A} \to \mathbf{A}' = \mathbf{A} + \nabla f, \tag{1.41}$$

where $f = f(\mathbf{r})$ is an arbitrary function of coordinates. This transformation, for the particular choice

$$f = -(1/2)(\mathbf{B} \times \mathbf{d}) \cdot \mathbf{r},$$

amounts to a shift $\mathbf{d}$ of origin of the coordinate frame. Accordingly, in order for eqs. (1.23)–(1.27) to make sense, the origin of the coordinate system must be chosen on the central charge Q. Under the change of gauge (1.41) the first–order energy (1.5′) must stay the same, which means that

$$\int dV\, \mathbf{J} \cdot \nabla f = 0. \tag{1.42}$$

In fact

$$\int dV\, \mathbf{J} \cdot \nabla f = \int dV\, \nabla \cdot (f\mathbf{J}) - \int dV\, f \nabla \cdot \mathbf{J}, \tag{1.43}$$

and, owing to the divergence theorem, the first volume integral on the r.h.s. is converted into a surface integral, vanishing due to the boundary conditions $\rho(\mathbf{r})$, $\mathbf{J}(\mathbf{r}) \to 0$ for $\mathbf{r} \to \infty$. Thus eqs. (1.42) and (1.43) are satisfied provided that the continuity equation for the stationary state,

$$\nabla \cdot \mathbf{J} = 0, \tag{1.44}$$

is fulfilled (compare eq. (1.21), assuming that ρ does not depend explicitly on time). Due to the arbitrary nature of f, one has in particular (for $f = x, y, z$)

$$\int dV\, \mathbf{J} = \mathbf{0}, \tag{1.45}$$

which, compare eq. (1.19), can be called the integral condition for charge conservation in the presence of static magnetic field.

Therefore invariance of the interaction energy in a translation of gauge of vector potential implies conservation of charge according to eq. (1.44) and *vice versa*. This result can be viewed within the general framework of the Nöther theorem [1], which asserts that every continuous symmetry characterizing a given mechanical system (in the present case invariance of the interaction energy to origin shift) implies a corresponding conservation constraint for that system. It is easily checked that equations (1.42) and (1.43) are obeyed by the Larmor current density. In particular, from the invariance of the second–order energy (1.31), one has immediately

$$\int dV\, \mathbf{J}_L \cdot \nabla f = 0.$$

The continuity equation in differential form $\nabla \cdot \mathbf{J}_L = 0$ is automatically fulfilled, compare for eq. (1.23), as $\mathbf{r}$ is always parallel to $\nabla\rho(\mathbf{r})$ in a central field. Similarly $\int dV \mathbf{J}_L = \mathbf{0}$ is satisfied by symmetry, as the average electric dipole of a spherical charge distribution vanishes.

5.1.5 Electronic current density induced by nuclear magnetic dipoles and nuclear magnetic coupling

Let us consider a molecule. The interaction energy due to Larmor precession between the external magnetic field and a magnetic dipole μ_I on nucleus I with position $\mathbf{R}_I$ is, compare eq. (1.28),

$$W^{\mu_I B} = -\frac{1}{c}\int dV \mathbf{A}^{\mu_I}\cdot\mathbf{J}_L = \mu_I\cdot\sigma_L(\mathbf{R}_I)\cdot\mathbf{B}, \tag{1.46}$$

where $\sigma_L(\mathbf{R}_I)$ is the magnetic shielding of nucleus I, and

$$\mathbf{A}^{\mu_I} = \mu_I\times\frac{\mathbf{r}-\mathbf{R}_I}{|\mathbf{r}-\mathbf{R}_I|^3} \tag{1.47}$$

is the vector potential at $\mathbf{r}$ due to the nuclear dipole. An obvious "interchange theorem" holds, that is,

$$W^{\mu_I B} = -\frac{1}{c}\int dV \mathbf{A}\cdot\mathbf{J}^{\mu_I}, \tag{1.48}$$

where

$$\mathbf{J}^{\mu_I} = \frac{e}{m_e c}\rho\mathbf{A}^{\mu_I} \tag{1.49}$$

is the Larmor–type current density induced by the nuclear magnetic dipole within the distribution of electrons with charge $-e$ and mass m_e. This definition complies with eqs. (1.23). The interaction energy (1.46) is $\approx 10^6$ times smaller than the *direct* interaction energy $-\mu_I\cdot\mathbf{B}$. Accordingly, the dimensionless shielding tensor components are customarily expressed in parts per million (p.p.m.).

The *direct* interaction energy of μ_I with another magnetic dipole, say μ_J on nucleus J, is

$$W_D^{\mu_I\mu_J} = -\mu_{I\alpha}B^J_{I\alpha} = -\mu_{J\alpha}B^I_{J\alpha}, \tag{1.50}$$

where

$$\mathbf{A}^J_I = \mu_J\times\frac{\mathbf{R}_{IJ}}{R^3_{IJ}} = -\mu_J\times\nabla_I R^{-1}_{IJ}, \tag{1.51}$$

$$\mathbf{R}_{IJ} = \mathbf{R}_I - \mathbf{R}_J, \qquad \nabla_I \equiv \frac{\partial}{\partial\mathbf{R}_I}, \tag{1.52}$$

and

$$B^J_{I\alpha} = \epsilon_{\alpha\beta\gamma}\nabla_{I\beta}A^J_{I\gamma} = -\mathcal{D}^{IJ}_{\alpha\beta}\mu_{J\beta} \tag{1.53}$$

is the average magnetic field on nucleus I arising from the nuclear magnetic dipole μ_J. The *direct coupling* tensor is defined

$$\mathcal{D}^{IJ}_{\alpha\beta} = \left(R^2_{IJ}\delta_{\alpha\beta} - 3R_{IJ\alpha}R_{IJ\beta}\right)R^{-5}_{IJ}. \tag{1.54}$$

The electron coupled, or *indirect*, interaction energy between the magnetic dipoles is

$$W^{\mu_I\mu_J} = -\frac{1}{c}\int dV\mathbf{A}^{\mu_J}\cdot\mathbf{J}^{\mu_I} = -\frac{1}{c}\int dV\mathbf{A}^{\mu_I}\cdot\mathbf{J}^{\mu_J}. \tag{1.55}$$

An *indirect coupling* tensor $\mathcal{K}^{IJ}_{\alpha\beta}$ can be defined to account for this interaction: by substituting for eqs. (1.47) and (1.49) in eq. (1.55) one finds

$$W^{\mu_I\mu_J} = \mu_{I\alpha}\mu_{J\beta}\mathcal{K}^{IJ}_{\alpha\beta} = -\mu_{I\alpha}B^n_{I\alpha}, \tag{1.56}$$

where

$$\mathcal{K}^{IJ}_{\alpha\beta} = \frac{e^2}{m_e c^2}\int dV\,\gamma(\mathbf{r})|\mathbf{r}-\mathbf{R}_I|^{-3}$$
$$|\mathbf{r}-\mathbf{R}_J|^{-3}\times[(r-R_I)_\gamma(r-R_J)_\gamma\delta_{\alpha\beta}-(r-R_J)_\alpha(r-R_I)_\beta]\,. \tag{1.57}$$

In terms of the second–rank current density tensor defined via

$$J^{\mu_I}_\alpha = \mathcal{J}^{\mu_{I\beta}}_\alpha\mu_{I\beta} \tag{1.58}$$

the coupling tensor becomes

$$\mathcal{K}^{IJ}_{\alpha\beta} = -\frac{1}{c}\epsilon_{\delta\alpha\gamma}\int dV\frac{(r-R_I)_\gamma}{|\mathbf{r}-\mathbf{R}_I|^3}\mathcal{J}^{\mu_{J\beta}}_\delta(\mathbf{r}). \tag{1.59}$$

Therefore the n molecular electrons perturbed by the nuclear magnetic dipole μ_I induce an average magnetic field on nucleus J

$$B^n_{J\alpha} = -\mathcal{K}^{JI}_{\alpha\beta}\mu_{I\beta}, \tag{1.60}$$

interacting with the probe $\mu_{J\alpha}$ according to eq. (1.56).

5.1.6 Hamiltonian

For a collection of charges the Larmor theorem can be recast in terms of classical Lagrangian [1, 3, 4] and Hamiltonian of the system. The Hamiltonian formulation of the problem is convenient for an extension to quantum mechanics [5–7]. As an example, let us consider a diamagnetic atom in the presence of the vector potential $\mathbf{A}(\mathbf{r})$ generating the uniform constant magnetic field $\mathbf{B}$. We neglect the motion of the nucleus. Within the stationary reference system K_s, the classical Hamiltonian for n electrons with charge $-e$, mass m_e, position $\mathbf{r}_i$, canonical momentum $\mathbf{p}_i$ and angular momentum $\mathbf{l}_i = \mathbf{r}_i\times\mathbf{p}_i, i = 1, 2...n$, (the subindex s is omitted to avoid clumsy notation) is, with obvious notation,

$$H = \frac{1}{2m_e}\sum_{i=1}^{n}\left(\mathbf{p}_i+\frac{e}{c}\mathbf{A}_i\right)^2 \equiv H_0 + H^{\mathbf{B}} + \frac{1}{2}H^{\mathbf{BB}}, \tag{1.61}$$

where V contains two–body Coulomb interactions depending only on the scalar distance between particles, and, compare eq. (1.1) for the definition of $\mathbf{L}$,

$$H_0 = \frac{1}{2m_e}\sum_{i=1}^{n}\mathbf{p}_i^2 + V, \tag{1.62}$$

$$H^{\mathbf{B}} = \frac{e}{2m_e c} B_\alpha L_\alpha, \tag{1.63}$$

$$H^{\mathbf{BB}} = \frac{e^2}{4m_e c^2} B_\alpha B_\beta \sum_{i=1}^{n} \left(r^2 \delta_{\alpha\beta} - r_\alpha r_\beta \right)_i . \tag{1.64}$$

Introducing, via eqs. (1.3) and (1.9), the precession angular velocity $\Omega_L = \frac{e}{2m_e c}\mathbf{B}$, one has

$$H^{\mathbf{B}} \equiv \Omega_{L\alpha} L_\alpha, \tag{1.65}$$

$$H^{\mathbf{BB}} \equiv \Omega_{L\alpha} \Omega_{L\beta} I_{\alpha\beta}, \tag{1.66}$$

where

$$I_{\alpha\beta} = m \sum_{i=1}^{n} \left(r^2 \delta_{\alpha\beta} - r_\alpha r_\beta \right)_i \tag{1.67}$$

is the moment of inertia of the electron distribution.

The Hamiltonian function can be rewritten with respect to a coordinate system K_r rotating with angular velocity Ω_L [3]:

$$H_r = H - \Omega_{L\alpha} L_\alpha, \tag{1.68}$$

hence, in terms of coordinates in the rotating system, the Hamiltonian has the simple form

$$H_r = H_0 + \frac{1}{2} H^{\mathbf{BB}}, \tag{1.69}$$

that is, first–order terms in $\mathbf{B}$ have disappeared. Again we conclude that, if $H^{\mathbf{BB}}$ is disregarded, then the behaviour of the electrons in the rotating reference system is the same as in the laboratory system in the absence of magnetic field.

However, we emphasize that $H^{\mathbf{BB}}$ is not negligible *per se*. In fact, in the present case of a diamagnetic atom, the spatial average of second–order Hamiltonian gives the contribution to the energy

$$W_L = \frac{e^2}{12mc^2} B^2 \sum_{i=1}^{n} \left(r_i^2 \right)^{Av},$$

so that, in accordance with eqs. (1.31) and (1.36), Larmor average susceptibility is defined

$$\chi_L^{Av} = -\frac{\partial^2 W_L}{\partial B^2},$$

and, more generally,

$$\chi_{L\alpha\beta} = -\frac{\partial^2 W_L}{\partial B_\alpha \partial B_\beta}. \tag{1.32$'$}$$

5.1.7 Limits and contradictions of the classical approach

In the previous sections we have shown how far one can apparently go using classical mechanics to understand diamagnetism. As matter of fact only the problem of a diamagnetic isolated atom can be formally solved, provided that the origin of the vector potential is fixed on the nucleus. A change of origin of the coordinate system, or more generally a change of gauge of the vector potential introduces serious shortcomings. The case of a molecule, where spherical symmetry is lost, becomes untractable: susceptibilities and nuclear magnetic shieldings evaluated via Larmor–type theories depend on the origin of the coordinate system. A step forward would be necessary to account for paramagnetism, requiring further *ad hoc* hypotheses: classical approaches cannot provide more than a qualitative explanation of magnetic phenomena. This is rather unsatisfactory; however, major drawbacks arise from internal contradictions affecting classical theory [8].

If a charge q, moving with velocity $\mathbf{v}$, is displaced by $d\mathbf{r}$ in time dt, the work done by the magnetic field is clearly vanishing: from (1.10)

$$\mathbf{F} \cdot d\mathbf{r} = \frac{q}{c}\mathbf{v} \times \mathbf{B} \cdot \mathbf{v}dt = 0.$$

Thus the energy of the charge is just the same as that in the absence of $\mathbf{B}$. For a system of charges this result apparently contradicts (1.5).

There is another difficulty, which cannot be solved on the basis of classical concepts. In fact, according to statistical mechanics, the probability that, at temperature T, a system will be at thermal equilibrium in a state of motion with energy W is $\propto \exp\left(-\frac{W}{kT}\right)$. If we assume that only one of such states can exist, we must conclude that a magnetic field has no effect on a classical system: at thermal equilibrium there will be no magnetic effect, no induced magnetic dipole, no current density, neither diamagnetism, nor paramagnetism.

This crucial argument seriously questions the possibility of really understanding magnetism by means of classical mechanics, and proves the need for a quantum mechanical theory of induced current densities.

5.2 QUANTUM MECHANICAL CURRENT DENSITY

5.2.1 Definition of current density from the Schrödinger equation

In 1926, shortly after Schrödinger famous paper [9] reporting the equation

$$H\Psi = i\hbar\frac{\partial}{\partial t}\Psi, \tag{2.1}$$

Madelung [10] showed that it can split up into real and imaginary components, yielding two "hydrodynamical" equations equivalent to (2.1), an equation of motion and an equation

of continuity. To this end let us simply assume that Ψ is relative to one particle of mass m and charge q. The Hamiltonian for the particle in the presence of electromagnetic field with vector potential $\mathbf{A}$ and scalar potential ϕ is

$$H = \frac{1}{2m}\pi^2 + q\phi, \tag{2.2}$$

where

$$\pi = \mathbf{p} - \frac{q}{c}\mathbf{A} \tag{2.3}$$

is the gauge–invariant mechanical momentum and $\mathbf{p} = -i\hbar\nabla$ is the canonical momentum. Throughout this section we will assume the Coulomb gauge $\nabla \cdot \mathbf{A} = 0$. [2] The norm

$$\mathcal{N} = \int d\tau |\Psi|^2 \tag{2.4}$$

is conserved in time. In fact from (2.1) and its complex conjugate,

$$H^*\Psi^* = -i\hbar\frac{\partial}{\partial t}\Psi^*, \tag{2.1'}$$

one has, owing to the Hermitian character of H,

$$\frac{d\mathcal{N}}{dt} = \frac{1}{i\hbar}\int d\tau [\Psi^*(H\Psi) - (H\Psi)^*\Psi] = 0. \tag{2.5}$$

Multiplying (2.1) on the left by Ψ^*, subtracting (2.1′) multiplied by Ψ and using (2.2) one finds an expression which can be rearranged in the form of a continuity equation,

$$\nabla \cdot \mathbf{j} + \frac{\partial}{\partial t}\gamma = 0, \tag{2.6}$$

where we interpret

$$\gamma = \Psi\Psi^* \tag{2.7}$$

as a probability density. The probability current density, also called number flux, $\mathbf{j}$ is defined

$$\mathbf{j} = \frac{1}{m}\Re(\Psi^*\pi\Psi) \equiv \mathbf{j}_{NL} + \mathbf{j}_L, \tag{2.8}$$

$$\mathbf{j}_L = -\frac{q}{mc}\mathbf{A}\Psi\Psi^*, \tag{2.9}$$

$$\mathbf{j}_{NL} = \frac{1}{m}\Re(\Psi^*\mathbf{p}\Psi) = \frac{\hbar}{m}\Im(\Psi^*\nabla\Psi) = \frac{\hbar}{m}\left(\Psi_R\nabla\Psi_I - \Psi_I\nabla\Psi_R\right), \tag{2.10}$$

assuming a complex form for the wavefunction, i.e.,

$$\Psi = \Psi_R + i\Psi_I.$$

[2] In the "radiation gauge" one also imposes $\phi = 0$. Alternatively one could introduce the Bloch gauge [11]: this choice is convenient in the case of a charge distribution, as it leads immediately to the multipole Hamiltonian.

The charge density is $\rho(\mathbf{r}) = q\gamma(\mathbf{r})$ and the charge current density is $\mathbf{J}(\mathbf{r}) = q\mathbf{j}(\mathbf{r})$. Thus, from (2.9), the quantum mechanical definition of Larmor charge current density analogous to the classical (I.23) becomes

$$\mathbf{J}_L = -\frac{q^2}{mc}\mathbf{A}\Psi\Psi^*, \tag{2.9′}$$

whereas $q\mathbf{j}_{NL}$ describes a non–Larmor current density arising from other mechanisms. Thus, in the case of electrons, the Larmor precession gives rise to the *diamagnetic* current

$$\mathbf{J}_d = -e\mathbf{j}_d, \tag{2.9″}$$

where $\mathbf{j}_d$ is obtained from (2.9) for $q = -e$. ¿From the non–Larmor density flow one has the *paramagnetic* current density $\mathbf{J}_p = -e\mathbf{j}_{NL}$.

The probability current density (2.8) is intrinsically arbitrary: one is always free to add any divergenceless vector $\mathbf{j}_{ADD} = \nabla \times \mathbf{W}$, since (2.6) is still satisfied. The continuity equation is much more general than the norm conservation (2.5). In fact, if

$$\Psi(\mathbf{r}, t) = \Phi(\mathbf{r}) \exp\left(-\frac{i}{\hbar}Et\right)$$

is a stationary solution to the Schrödinger equation with energy eigenvalue E, then the norm is obviously conserved in time for a bound system, whereas norm conservation has no meaning for unbound systems, since Ψ is no longer square–integrable. In both cases, however, the continuity equation is valid and, if γ does not depend explicitly on time, then $\nabla \cdot \mathbf{j} = 0$.

5.2.2 The hydrodynamical formulation of quantum mechanics

The hydrodynamical approach [10, 12–26] resembles classical mechanics; this becomes transparent by expressing the wavefunction in the semiclassical form [7]

$$\Psi(\mathbf{r}, t) = \gamma^{\frac{1}{2}}(\mathbf{r}, t) \exp\left[\frac{i}{\hbar}S(\mathbf{r}, t)\right], \tag{2.11}$$

$$\Psi_R = \gamma^{\frac{1}{2}} \cos\frac{S}{\hbar}, \qquad \Psi_I = \gamma^{\frac{1}{2}} \sin\frac{S}{\hbar}. \tag{2.12}$$

If Ψ describes a stationary state, the action $S = \hbar\Im(\ln\Psi)$ satisfies the relationship

$$\frac{\partial S}{\partial t} = -E,$$

and

$$\Psi = \gamma^{\frac{1}{2}} \exp\left(-\frac{i}{\hbar}Et\right).$$

Ψ and $\nabla\Psi$ are assumed continuous and single–valued for any $\mathbf{r}$, except at points where the potential is infinite. Corresponding to those points, Ψ is still continuous, but $\nabla\Psi$ may be

discontinuos. Consequently, $\gamma^{\frac{1}{2}}$ is continuous everywhere and $\nabla\gamma^{\frac{1}{2}}$ is continuous except at points where $\Psi = 0$. When $\Psi = 0$, neither the phase

$$\frac{S}{\hbar} = \arctan\frac{\Psi_I}{\Psi_R} \pm \pi n', \qquad n' = 0, 1, 2 \ldots, \tag{2.13}$$

nor its gradient

$$\nabla\left(\frac{S}{\hbar}\right) = \left(\Psi_R^2 + \Psi_I^2\right)^{-1}(\Psi_R\nabla\Psi_I - \Psi_I\nabla\Psi_R) = \Im(\nabla \ln \Psi), \tag{2.14}$$

are well defined. In the domain where Ψ is not vanishing $\nabla\left(\frac{S}{\hbar}\right)$ is well defined, but according to (2.13), the phase is only defined to multiples of π. However, a prescription for determining the phase change in going around a loop has been given by Hirschfelder *et al.* [20, 21].

Using ansatz (2.11), one finds from (2.1) and (2.2), by separating real and imaginary parts, the "quantum correction" to the potential,

$$V_{qu} = -\frac{\hbar^2}{2m}\gamma^{-\frac{1}{2}}\nabla^2\gamma^{\frac{1}{2}}, \tag{2.15}$$

satisfying

$$\frac{1}{2m}(\nabla S)^2 - \frac{q}{mc}\mathbf{A}\cdot\nabla S + \frac{q^2}{2mc^2}A^2 + q\phi + V_{qu} + \frac{\partial S}{\partial t} = 0, \tag{2.16}$$

and

$$\frac{\partial}{\partial t}\gamma^{\frac{1}{2}} + \frac{1}{2m}\gamma^{\frac{1}{2}}\nabla^2 S + \frac{1}{m}\left(\nabla S - \frac{q}{c}\mathbf{A}\right)\cdot\nabla\gamma^{\frac{1}{2}} = 0. \tag{2.17}$$

In the classical limit for $\hbar \to 0$, V_{qu} vanishes and relationship (2.16) becomes the Hamilton–Jacobi equation of motion, which is formally obtained from the Hamilton equation by putting

$$H = -\frac{\partial S}{\partial t}, \qquad \nabla S = \mathbf{p}. \tag{2.18}$$

Multiplying (2.17) by $2\gamma^{\frac{1}{2}}$, one can rewrite it in the form

$$\frac{\partial\gamma}{\partial t} + \nabla\cdot\left[\frac{1}{m}\gamma\left(\nabla S - \frac{q}{c}\mathbf{A}\right)\right] = 0. \tag{2.19}$$

It can be easily shown that (2.19) is the same as the continuity equation (2.6). In fact, from (2.9) and (2.10), one has

$$\mathbf{j}_{NL} = \frac{\hbar}{m}\Im(\Psi^*\nabla\Psi) = \frac{1}{m}\gamma\nabla S, \tag{2.20}$$

$$\mathbf{j}_L = -\frac{q}{mc}\mathbf{A}\gamma. \tag{2.21}$$

In a gauge transformation

$$\mathbf{A} \to \mathbf{A}' = \mathbf{A} + \nabla f(\mathbf{r}, t), \tag{2.22}$$

$$\Psi \to \Psi' = \Psi \exp\left(\frac{iq}{\hbar c} f\right), \tag{2.23}$$

$$S \to S' = S + \frac{q}{c} f, \tag{2.24}$$

and one finds from (2.20) and (2.21)

$$\mathbf{j}'_{NL} = \mathbf{j}_{NL} + \frac{q}{mc} \gamma \nabla f, \tag{2.25}$$

$$\mathbf{j}'_{L} = \mathbf{j}_{L} - \frac{q}{mc} \gamma \nabla f, \tag{2.26}$$

that is, Larmor and non–Larmor contributions to $\mathbf{j}$ are not uniquely defined, and only the total probability current density is left invariant. Choosing

$$f = -\frac{c}{q} S$$

one has in particular

$$\mathbf{j}' = \mathbf{j}_L, \tag{2.27}$$

that is, the non–Larmor current density has been formally annihilated. This result is valid in those points where $S(\mathbf{r}, t)$ is well defined, so that the irrotational vector ∇S exists. Those points lie outside of the nodal regions of Ψ; in other words, the regime is of the Larmor type in nodeless regions. In a node $\mathbf{r}_0$ of Ψ, ∇S is neither continuous nor irrotational, that is

$$\nabla \times \nabla S(\mathbf{r}_0, t) \neq \mathbf{0}$$

in general. Hence a physically meaningful non–Larmor current only exists about nodes of Ψ.

¿From the quantum analog of the classic formula

$$\mathbf{j} = \gamma \mathbf{v}, \tag{2.28}$$

one defines the Madelung–Landau–London [10, 12, 13] *local mean velocity*

$$\mathbf{v} = \mathbf{v}_{NL} + \mathbf{v}_L,$$

$$\mathbf{v}_{NL} = \frac{1}{m} \nabla S = \frac{\hbar}{m} \left(\Psi_R^2 + \Psi_I^2\right)^{-1} (\Psi_R \nabla \Psi_I - \Psi_I \nabla \Psi_R),$$

$$\mathbf{v}_L = -\frac{q}{mc} \mathbf{A}. \tag{2.29}$$

This definition of the Larmor velocity can be compared with (I.26). We observe that $\mathbf{v}(\mathbf{r}, t)$ is not defined in the nodal regions of Ψ and that the non–Larmor contribution is identically vanishing in the case of real wavefunctions.

Hirschfelder *et al.* [20, 23] have introduced the idea of *imaginary* mean local velocity, which is quite useful to rewrite the quantum correction V_{qu} to the potential energy in a heuristic form. The mean local mechanical momentum can be written

$$\Psi^{-1}\pi\Psi = \frac{m\mathbf{j}}{\gamma} - \frac{i\hbar}{2}\nabla \ln \gamma = m\mathbf{v} + im\mathbf{v}_I, \tag{2.30}$$

so that

$$\mathbf{v}_I = -\frac{\hbar}{2m}\nabla \ln \gamma \tag{2.31}$$

is interpreted as imaginary mean local velocity. The quantum correction (2.15) to the potential energy can be written

$$V_{qu} = -\frac{1}{2}mv_I^2 + \frac{1}{2}\hbar\nabla \cdot \mathbf{v}_I. \tag{2.32}$$

¿From (2.19) and (2.29) the continuity equation becomes

$$\frac{\partial\gamma}{\partial t} + \nabla \cdot (\gamma\mathbf{v}) = 0. \tag{2.6′}$$

Owing to (2.19), the equation of motion (2.16) can be written

$$\frac{1}{2}mv^2 + \frac{\partial S}{\partial t} + q\phi + V_{qu} = 0. \tag{2.33}$$

Let us operate with ∇ on the l.h.s. of (2.33) and use the expressions for the electric field

$$\mathbf{E} = -\nabla\phi - \frac{1}{c}\frac{\partial}{\partial t}\mathbf{A}, \tag{2.34}$$

and for the magnetic field

$$\mathbf{B} = \nabla \times \mathbf{A}. \tag{2.35}$$

The total differential for any vector $\mathbf{W} = \mathbf{W}(\mathbf{r}, t)$ is

$$dW_\alpha = \frac{\partial W_\alpha}{\partial r_\beta}dr_\beta + \frac{\partial W_\alpha}{\partial t}dt,$$

so that

$$\frac{d\mathbf{W}}{dt} = \frac{\partial\mathbf{W}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{W}.$$

Using

$$\frac{1}{2}\nabla(\mathbf{v} \cdot \mathbf{v}) = (\mathbf{v} \cdot \nabla)\mathbf{v} + \mathbf{v} \times (\nabla \times \mathbf{v}),$$

one finds, in nodeless regions,

$$m\frac{d\mathbf{v}}{dt} = q\left(\mathbf{E} + \frac{1}{c}\mathbf{v} \times \mathbf{B}\right) - \nabla V_{qu} \tag{2.36}$$

which, in the classical limit becomes the Newton equation of motion for a particle with charge q acted upon by the Lorentz force [14].

5.2.3 The vorticity condition

Formulae (2.19) and (2.36) are a system of four hydrodynamical–like equations for compressible fluids. This hydrodynamical description is completely equivalent to (2.1) if and only if the circulation of $\mathbf{v}$ satisfies the quantization condition [15–26]

$$\triangle\left(\frac{S}{\hbar}\right)=\oint d\mathbf{r}\cdot\nabla\left(\frac{S}{\hbar}\right)=\frac{m}{\hbar}\oint\mathbf{v}\cdot d\mathbf{r}+\frac{q}{\hbar c}\oint\mathbf{A}\cdot d\mathbf{r}=2\pi n',n'=0,\pm1,\pm2\ldots, \quad (2.37)$$

where $\triangle\left(\frac{S}{\hbar}\right)$ is the change in phase of Ψ on traversing the loop once (the loop must not pass through a node of Ψ, since neither S nor ∇S are well defined there). This result follows immediately from the fact that the phase of Ψ at a certain point is only defined up to an integer multiple of 2π. ¿From the quantization condition one has that the loop of circulation can be arbitrarily deformed and shrunk to a circle of radius zero, in which $\triangle\left(\frac{S}{\hbar}\right)=0$. This is consistent with the fact that, using the Stokes theorem in (2.37), one must have

$$\nabla\times\nabla S=m\nabla\times\mathbf{v}+\frac{q}{c}\mathbf{B}=\mathbf{0}, \quad (2.38)$$

outside of the nodal regions. The quantization condition (2.37) can be reformulated as a vorticity condition [14–23]

$$\oint\mathbf{v}\cdot d\mathbf{r}=\frac{h}{m}n'-\frac{q}{mc}\iint_{\mathbf{s}}\mathbf{B}\cdot d\mathbf{s}, \quad (2.37')$$

where $d\mathbf{s}=\mathbf{n}_s ds$, ds is an element of the surface enclosed by the loop of circulation and $\mathbf{n}_s$ is the unit vector locally perpendicular to ds, and

$$n'=\frac{1}{2\pi}\iint_{\mathbf{s}}\Im\{\nabla\times\nabla\ln\Psi\}\cdot d\mathbf{s}. \quad (2.39)$$

Outside of nodal regions of Ψ, $\nabla\ln\Psi$ exists and

$$\nabla\times\nabla\ln\Psi=0=n',$$

that is, there is a vortical Larmor regime. In the domains where $\Psi=0$, $\nabla\ln\Psi$ is not defined, $\nabla\times\nabla\ln\Psi\neq0$ and a non–Larmor circulation, see also the discussion from (2.25) to (2.27), adds to the Larmor precession.

As an example of circulation (2.37), let us consider the (unperturbed) hydrogen stationary electronic states

$$\Psi\equiv\Psi_{\underline{nlm}}(\mathbf{r})=f(r,\theta)\exp(i\underline{m}\phi).$$

From

$$\mathbf{v}\equiv\mathbf{v}_{NL}=\frac{\hbar}{m}\Im(\nabla\ln\Psi),$$

expressing ∇ in polar coordinates, and indicating by $\mathbf{u}_\phi$ the azimuthal unit vector, one finds

$$\oint\mathbf{v}\cdot d\mathbf{r}\equiv\frac{\hbar}{m}\int_0^{2\pi}\Im\left(\nabla\ln\Psi\right)\cdot\mathbf{u}_\phi r\sin\theta\,d\phi=\frac{\hbar}{m}\underline{m}\int_0^{2\pi}d\phi=\frac{h}{m}\underline{m},$$

that is, the circulation number is just the familiar magnetic quantum number $\underline{m}$.

It is convenient to introduce the idea of first–order current density tensor as in the classical case (I.37), via the series

$$J_\alpha(\mathbf{r}) = J_\alpha^{(0)}(\mathbf{r}) + \mathcal{J}_\alpha^{B_\beta}(\mathbf{r})B_\beta + \dots \tag{2.40}$$

The magnetic susceptibility and the nuclear magnetic shielding at nucleus I, with position $\mathbf{R}_I$, can be rewritten, compare with eqs. (I.39) and (I.40),

$$\chi_{\alpha\delta} = \frac{1}{2c}\epsilon_{\alpha\beta\gamma}\int dV r_\beta \mathcal{J}_\gamma^{B_\delta}(\mathbf{r}), \tag{2.41}$$

$$\sigma_{\alpha\delta}^I = -\frac{1}{c}\epsilon_{\alpha\beta\gamma}\int dV \frac{r_\beta - R_{I\beta}}{|\mathbf{r}-\mathbf{R}_I|^3}\mathcal{J}_\gamma^{B_\delta}(\mathbf{r}). \tag{2.42}$$

As discussed by Hirschfelder [26], the probability density and the probability current density are *subobservables*, that is, they are respectively the expectation value of the operators

$$\gamma_{Op}(\mathbf{r}_0) = \delta(\mathbf{r}-\mathbf{r}_0), \tag{2.43}$$

$$\mathbf{j}_{Op}(\mathbf{r}_0) = \frac{1}{2m}\left[\pi,\delta\right]_+. \tag{2.44}$$

Accordingly, the scalar function $\gamma(\mathbf{r})$ and the vector field $\mathbf{j}(\mathbf{r})$ can be interpreted as classical quantities. In particular, one can introduce the notion of trajectory in the $\mathbf{j}$ field as a function of position $\mathbf{r}$. This will be useful to visualize the streamlines.

The real autonomous system of differential equations for the trajectory in the $\mathbf{v}$ field,

$$\frac{d\mathbf{r}}{dt} = \mathbf{v}, \tag{2.45}$$

is equivalent to

$$\frac{dx}{v_x} = \frac{dy}{v_y} = \frac{dz}{v_z}. \tag{2.45$'$}$$

This equation can be easily integrated to get the streamlines in the $\mathbf{v}$ field, but their quantum mechanical meaning would be difficult to assess for the following reasons. We have seen that $\mathbf{v}_{NL}$ is zero in the case of real wavefunctions, for instance, in the absence of magnetic field for diamagnetic systems, that are even under time reversal. Bohm [27] explains it by stating that "the absence of motion is possible because the applied force is balanced by the quantum mechanical force $-\nabla V_{qu}$ produced by the Schrödinger field acting on its own particle". In any event, the vector $\mathbf{v}$, interpreted as local mean velocity, is not a subobservable, that is, there is no linear Hermitian operator for which it is the expectation value. This limits the physical meaning of $\mathbf{v}$; as a matter of fact, because of the uncertainty principle, one should not attach too much significance to the behaviour of $\mathbf{v}$ in regions whose dimensions are small compared to the de Broglie wavelength.

However, as $\mathbf{j} = \gamma\mathbf{v}$, the vorticity condition (2.37') for $\mathbf{v}$ may be helpful to predict the existence of vortices in the $\mathbf{j}$ field in the vicinity of the nodes of Ψ.

In order for a nodal region to have a non vanishing circulation, it must be capable of trapping a loop [19]. In other words, it would be impossible to deform the loop of circulation into a path excluding a node of Ψ. This can only happen if the nodal manifold is boundariless, for instance, an infinite line, or a close curve, or any topologically equivalent region, endless ribbon or rod. Thus we are left with the possibility of either *axial* vortices, rotating around nodal manifolds which extend to the boundaries of space, or *toroidal* vortices flowing up through the centre and down around the sides of a closed nodal line.

The considerations we have made so far for one particle cannot be easily generalized to the case of an $N-$particle system. In practice it would be very difficult to determine the topology of $(3N-2)$ dimensional nodal manifolds associated with a multivalued phase function in $3N-$dimensional configuration space. Therefore, it is expedient to reduce the dimensionality of the configuration space to three dimensions by introducing probability density and current density matrices and their natural expansions, which lead to a component analysis.

The $N-$particle current density field can thus be studied by analyzing a mixture of separate one–particle contributions provided by distinct natural spin–orbitals. In this hydrodynamical representation the many–components fluid is compressible, viscous and rotational. Different components have different velocities, so that there may be diffusion: the continuity equation (2.6) is not, in general, fulfilled for each separate component. This may sometimes, limit the *a priori* analysis of the $N-$particle $\mathbf{j}$ field. Other methods are to be sought to predict the general features of the current density, that is trajectories and singularities. Powerful tools are provided by group theory and by the theory of differential equations [28].

5.3 MOLECULAR MAGNETIC PROPERTIES AND ELECTRONIC CURRENT DENSITY

5.3.1 Quantum mechanical current density in a molecule

The n-electron wavefunction of a molecule $\Psi(\mathbf{x}_1, \mathbf{x}_2 \ldots \mathbf{x}_n)$ is written in terms of space and spin coordinates $\mathbf{x}_i = \mathbf{r}_i \times \mathbf{s}_i$, and the (probability) density matrix is defined [29]

$$P_1\left(\mathbf{r};\mathbf{r}'\right) = n \int d\mathbf{x}_2 \ldots d\mathbf{x}_n \, \Psi(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n)\Psi^*(\mathbf{r}', \mathbf{x}_2 \ldots \mathbf{x}_n). \tag{3.1}$$

The electronic current density is introduced in the form [29]

$$\mathbf{J}(\mathbf{r}) = -\frac{e}{m_e}\Re\left[\pi P_1\left(\mathbf{r};\mathbf{r}'\right)\right]_{\mathbf{r}'=\mathbf{r}}, \tag{3.2}$$

where the mechanical momentum operator (2.3) for one electron becomes

$$\pi = \mathbf{p} + \frac{e}{c}\mathbf{A}. \tag{3.3}$$

In the presence of a space–uniform, time–independent magnetic field with flux $\mathbf{B}$, and of a permanent magnetic dipole μ_I on the I–th nucleus, $\mathbf{A} = \mathbf{A}^{\mathbf{B}} + \mathbf{A}^{\mu_I}$, with

$$\mathbf{A}^{\mathbf{B}} = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{r}_0), \quad \mathbf{A}^{\mu_I} = \mu_I \times \frac{\mathbf{r} - \mathbf{R}_I}{|\mathbf{r} - \mathbf{R}_I|^3}, \tag{3.4}$$

(the origin $\mathbf{r}_0$ is arbitrary and can be put equal to $\mathbf{0}$ without loss of generality). The n-electron wavefunction is conveniently written as a perturbation expansion

$$\Psi = \Psi_0 + \mathbf{\Psi}^{\mathbf{B}} \cdot \mathbf{B} + \mathbf{\Psi}^{\mu_I} \cdot \mu_I + \cdots. \tag{3.5}$$

¿From Rayleigh-Schrödinger perturbation theory, the first–order electronic wavefunction in the presence of magnetic field is

$$\left|\mathbf{\Psi}^{\mathbf{B}}\right\rangle = -\frac{e}{2m_e c\hbar}\sum_{j\neq a}\omega_{ja}^{-1}|j\rangle\langle j|\mathbf{L}|a\rangle, \tag{3.6}$$

denoting by $|a\rangle \equiv |\Psi_0\rangle$ the reference state $\left|\Psi_a^{(0)}\right\rangle$. As the perturbations arising from the external magnetic field and the intrinsic nuclear moment are represented by purely imaginary terms in the first–order interaction Hamiltonian, there is no first–order correction to the diagonal elements of density matrix (3.1), *i.e.*, the electronic charge distribution is not modified: stationary currents are induced. ¿From eqs. (3.2)–(3.5), the electronic current density can be written as a sum of paramagnetic and diamagnetic contributions,

$$\mathbf{J}^{\mathbf{B}} = \mathbf{J}_p^{\mathbf{B}} + \mathbf{J}_d^{\mathbf{B}}, \tag{3.7}$$

where

$$\mathbf{J}_d^{\mathbf{B}}(\mathbf{r}) = -\frac{e^2}{2m_e c}\mathbf{B} \times \mathbf{r}\gamma(\mathbf{r}), \tag{3.8}$$

is related to the diagonal (probability) density

$$\gamma(\mathbf{r}) = P_1\left(\mathbf{r};\mathbf{r}\right), \tag{3.9}$$

and the paramagnetic contribution is written via eq. (3.6)

$$\mathbf{J}_p^{\mathbf{B}}(\mathbf{r}) = -\frac{ne}{m_e}\int d\mathbf{x}_2 \ldots d\mathbf{x}_n \Big[\mathbf{B} \cdot \mathbf{\Psi}^{\mathbf{B}*}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n)\mathbf{p}\Psi_0(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n)$$

$$+ \Psi_0^*(\mathbf{r}, \mathbf{x}_2 \ldots \mathbf{x}_n)\mathbf{p}\mathbf{B} \cdot \mathbf{\Psi}^{\mathbf{B}}(\mathbf{r}, \mathbf{x}_2, \ldots \mathbf{x}_n)\Big]. \tag{3.10}$$

The integral condition for charge–current conservation (I.45) becomes, in the present case of n electrons,

$$\int J_\alpha^{\mathbf{B}} d\mathbf{r} = 0, \tag{3.11}$$

which, according to eq. (3.7), can be recast in the form [30]

$$\int \left(J^{\mathbf{B}}_{d\alpha} + J^{\mathbf{B}}_{p\alpha} \right) d\mathbf{r} = \frac{e^2}{2m_e^2 c} \left[(P_\alpha, L_\beta)_{-1} - m_e \epsilon_{\alpha\beta\gamma} \langle a | R_\gamma | a \rangle \right] = 0, \tag{3.12}$$

where

$$(P_\alpha, L_\beta)_{-1} \equiv \frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \Re \left(\langle a | P_\alpha | j \rangle \langle j | L_\beta | a \rangle \right). \tag{3.13}$$

Accordingly, conservation of pure paramagnetic current density along the direction of the field is guaranteed by symmetry. Identity (3.12) can be proven directly via the off-diagonal hypervirial relation

$$\langle j | \mathbf{P} | a \rangle = i m_e \omega_{ja} \langle j | \mathbf{R} | a \rangle. \tag{3.14}$$

In analogy to eqs. (I.37) and (2.40) a second–rank current density tensor is introduced via

$$J^{\mathbf{B}}_\alpha = \mathcal{J}^{B_\beta}_\alpha B_\beta, \tag{3.15}$$

so that magnetic susceptibility and nuclear magnetic shielding are again defined

$$\chi_{\alpha\delta} = \frac{1}{2c} \epsilon_{\alpha\beta\gamma} \int r_\beta \mathcal{J}^{B_\delta}_\gamma(\mathbf{r}) d\mathbf{r}, \tag{3.16}$$

$$\sigma^I_{\alpha\delta} = -\frac{1}{c} \epsilon_{\alpha\beta\gamma} \int \frac{r_\beta - R_{I\beta}}{|\mathbf{r} - \mathbf{R}_I|^3} \mathcal{J}^{B_\delta}_\gamma(\mathbf{r}) d\mathbf{r}. \tag{3.17}$$

These relationships are formally identical to eqs. (I.39), (I.40) and to eqs. (2.41), (2.42). It should be emphasized, however, that eqs. (3.16) and (3.17) are now written in terms of an $N-$electron current density accounting for both Larmor and non–Larmor contributions.

5.3.2 Invariance of current density to a change of coordinate system

As observed in the one–particle case, total current density (3.7) and magnetic properties (3.16) and (3.17) must be invariant to an arbitrary gauge transformation of the vector potential, see the first of eqs. (3.4),

$$\mathbf{A}^{\mathbf{B}'} \rightarrow \mathbf{A}^{\mathbf{B}''} = \mathbf{A}^{\mathbf{B}'} + \nabla f, \qquad \mathbf{A}^{\mathbf{B}'} = \frac{1}{2} \mathbf{B} \times (\mathbf{r} - \mathbf{r}'), \tag{3.18}$$

where $f = f(\mathbf{r})$ is an arbitrary function well-behaved for $\mathbf{r} \rightarrow \infty$. A shift of the origin of coordinates by a vector $\mathbf{d}$,

$$\mathbf{r}' \rightarrow \mathbf{r}'' = \mathbf{r}' + \mathbf{d}, \tag{3.19}$$

is equivalent to a gauge transformation (3.18) where $f = (\mathbf{r}'' - \mathbf{r}') \cdot \mathbf{A}^{\mathbf{B}'}$. This origin translation does not affect total values, but diamagnetic and paramagnetic contributions to current density (3.7), and to properties (3.16) and (3.17), transform into each other.

The important connection between continuity equation and gauge independence has been already recalled in Chapter I: in fact, constraint (3.12) also insures invariance of

magnetic susceptibility to a gauge translation [30–33]. Total current density is a vector function of position, *i.e.*, $\mathbf{J}^{\mathbf{B}} = \mathbf{J}^{\mathbf{B}}(\mathbf{r})$, where the origin can be arbitrarily chosen. In an arbitrary change of gauge, in particular in a change of coordinate system (3.19), this function stays the same whenever the wavefunction Ψ, compare eqs. (3.1) and (3.2), is an exact eigenstate to a model Hamiltonian [30],

$$\mathbf{J}^{\mathbf{B}}(\mathbf{r}-\mathbf{r}'') = \mathbf{J}^{\mathbf{B}}(\mathbf{r}-\mathbf{r}') + \mathbf{J}_d^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}(\mathbf{r})$$
$$+\mathbf{J}_p^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}) = \mathbf{J}^{\mathbf{B}}(\mathbf{r}-\mathbf{r}') \equiv \mathbf{J}^{\mathbf{B}}(\mathbf{r}), \tag{3.20}$$

(this notation implies that diamagnetic and paramagnetic components, which depend on the coordinate system, are evaluated corresponding to different origins). Consistent with eq. (3.20), the diamagnetic contribution to the current density transforms to [31]

$$\mathbf{J}_d^{\mathbf{B}}(\mathbf{r}-\mathbf{r}'') = \mathbf{J}_d^{\mathbf{B}}(\mathbf{r}-\mathbf{r}') + \mathbf{J}_d^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}), \tag{3.21}$$

where

$$\mathbf{J}_d^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}) = -\frac{e^2}{2m_e c}(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}\gamma(\mathbf{r}), \tag{3.22}$$

and the paramagnetic contribution transforms to

$$\mathbf{J}_p^{\mathbf{B}}(\mathbf{r}-\mathbf{r}'') = \mathbf{J}_p^{\mathbf{B}}(\mathbf{r}-\mathbf{r}') + \mathbf{J}_p^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}), \tag{3.23}$$

where

$$\mathbf{J}_p^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}) = -\frac{e}{m_e} n \int d\mathbf{x}_2 \ldots d\mathbf{x}_n \Big[(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}\cdot\boldsymbol{\Psi}^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}*}\mathbf{p}\Psi_0$$
$$+ \Psi_0^*\mathbf{p}(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}\cdot\boldsymbol{\Psi}^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}\Big], \tag{3.24}$$

introducing the perturbed function

$$\left|\boldsymbol{\Psi}^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}\right\rangle = -\frac{e}{2m_e c\hbar}\sum_{j\neq a}\omega_{ja}^{-1}|j\rangle\langle j|\mathbf{P}|a\rangle. \tag{3.25}$$

It is worth noticing that current density terms (3.22) and (3.24) do not depend on the origin. The condition for invariance of total current density is therefore

$$\mathbf{J}_p^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}} + \mathbf{J}_d^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}} = \mathbf{0}, \tag{3.26}$$

which can be proven directly via hypervirial relation (3.14).

5.3.3 Annihilation of diamagnetic contribution to current density

Transformed diamagnetic current density term, $\mathbf{J}_d^{\mathbf{B}}(\mathbf{r}-\mathbf{r}'')$, can be formally annihilated for every point $\mathbf{r}$, all over the molecular domain, by choosing that point as origin, *i.e.*, setting $\mathbf{r}'' = \mathbf{r}$, compare eq. (3.21), so that

$$\mathbf{J}_d^{\mathbf{B}}(\mathbf{r}-\mathbf{r}') = -\mathbf{J}_d^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}), \tag{3.27}$$

within a scheme described as "continuous trasformation of origin of the current density", see Refs. [35, 31–34]. This procedure amounts to choosing a function $\mathbf{d}(\mathbf{r}) = \mathbf{r}$ instead of a constant vector $\mathbf{d}$ in eq. (3.19). As a matter of fact, this pointwise procedure is not necessary, as the problem can be given a fully analytical solution via equations in closed form [31]. As the diamagnetic term is set to zero, this procedure is indicated by the acronym CTOCD–DZ. Total current becomes completely paramagnetic in form, and contains two terms defined in the former coordinate system, *i.e.*,

$$\mathbf{J}^{\mathbf{B}}(\mathbf{r}) = \mathbf{J}_p^{\mathbf{B}}(\mathbf{r} - \mathbf{r}') + \mathbf{J}_p^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}), \tag{3.28}$$

where, compare eq. (3.24),

$$\mathbf{J}_p^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}) = -\frac{en}{m_e}\int d\mathbf{x}_2 \dots d\mathbf{x}_n \Big[(\mathbf{r}'' - \mathbf{r}') \times \mathbf{B} \cdot \mathbf{\Psi}^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}*}\mathbf{p}\Psi_0 + \Psi_0^*\mathbf{p}(\mathbf{r}'' - \mathbf{r}') \times \mathbf{B} \cdot \mathbf{\Psi}^{(\mathbf{r}''-\mathbf{r}')\times\mathbf{B}}\Big]_{\mathbf{r}''=\mathbf{r}}, \tag{3.29}$$

(this notation means that $\mathbf{r}''$ is put equal to $\mathbf{r}$ after operating with $\mathbf{p}$). As total current density is an invariant, mapped onto itself by any transformation, comparison between eqs (3.7) and (3.28) necessarily implies (which is not useful as a calculation recipe) that

$$\mathbf{J}_p^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}(\mathbf{r}) = \mathbf{J}_d^{\mathbf{B}}(\mathbf{r} - \mathbf{r}'), \tag{3.30}$$

for every $\mathbf{r}$. This relationship can be directly proven via eqs. (3.8) and (3.29), using identity (3.14), for every plane perpendicular to $\mathbf{B}$, where the original diamagnetic circulation takes place. On the other hand, formal replacement according to eq. (3.30) of diamagnetic term (3.8) with a paramagnetic one in eq. (3.28), introduces a spurious (paramagnetic) component along the inducing magnetic field. In fact, the parallel component in eq. (3.29) is unphysical and must be discarded. Anyway, this extra current automatically fulfills conservation condition (3.11), if off–diagonal hypervirial relationship (3.14) is satisfied. Let us assume that the external magnetic is aligned with the z axis, *i.e.*, $\mathbf{B} \equiv \mathbf{e}_3 B$, then

$$J_{pz}^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}} = -\frac{neB}{m_e}\int d\mathbf{x}_2 \dots d\mathbf{x}_n \times \Big[(y - y')\left(\Psi_x^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}*}p_z\Psi_0 + \Psi_0^* p_z \Psi_x^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}\right) - (x - x')\left(\Psi_y^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}*}p_z\Psi_0 + \Psi_0^* p_z \Psi_y^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}\right)\Big]. \tag{3.31}$$

This integral contains vanishing tensors of the form

$$\left(P_x, \sum_{i=1}^n y_i p_{iz}\right)_{-1} = \frac{1}{\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\Re\left(\langle a|P_x|j\rangle \left\langle j\left|\sum_{i=1}^n y_i p_{iz}\right|a\right\rangle\right) = -\frac{\imath m_e}{\hbar}\left\langle a\left|\left[R_x, \sum_{i=1}^n y_i p_{iz}\right]\right|a\right\rangle = 0, \tag{3.32}$$

so that

$$\int J_{pz}^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}} d\mathbf{r} = \frac{e^2 B}{2m_e^2 c}\left[\left(P_x, \sum_{i=1}^n y_i p_{iz}\right)_{-1} - \left(P_y, \sum_{i=1}^n x_i p_{iz}\right)_{-1}\right]$$

$$= -\frac{\imath e^2 B}{2m_e c\hbar}\left\{\left\langle a\left|\left[R_x, \sum_{i=1}^{n} y_i p_{iz}\right]\right|a\right\rangle + \left\langle a\left|\left[R_y, \sum_{i=1}^{n} x_i p_{iz}\right]\right|a\right\rangle\right\} = 0. \tag{3.33}$$

A more general relationship, consistent with constraint (3.12),

$$\int J_{p\alpha}^{(\mathbf{r}-\mathbf{r}')\times\mathbf{B}}\, d\mathbf{r} = \int J_{d\alpha}^{\mathbf{B}}\, d\mathbf{r} = -\frac{e^2}{2m_e c}\epsilon_{\alpha\beta\gamma} B_\beta \left\langle a|R_\gamma|a\right\rangle, \tag{3.34}$$

is found using eq. (3.14).

Within the notation of previous papers [30–34], the magnetic susceptibility and the magnetic shielding of the I-th nucleus are conventionally defined as sums of paramagnetic and diamagnetic contributions,

$$\chi_{\alpha\beta}^{\mathrm{p}} = \frac{e^2}{4c^2 m_e^2 \hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\Re\left(\langle a|L_\alpha|j\rangle\langle j|L_\beta|a\rangle\right), \tag{3.35}$$

$$\chi_{\alpha\beta}^{\mathrm{d}} = -\frac{e^2}{4m_e c^2}\left\langle a\left|\sum_{i=1}^{n}\left(r_\gamma^2\delta_{\alpha\beta} - r_\alpha r_\beta\right)_i\right|a\right\rangle, \tag{3.36}$$

$$\sigma_{\alpha\beta}^{\mathrm{p}I} = -\frac{e^2}{2m_e^2 c^2\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\Re(\langle a|M_{I\alpha}^n|j\rangle\,\langle j|L_\beta|\rangle), \tag{3.37}$$

$$\sigma_{\alpha\beta}^{\mathrm{d}I} = \frac{e}{2m_e c^2}\left\langle a\left|\sum_{i=1}^{n}\left(r_{i\gamma}E_{I\gamma}^i\delta_{\alpha\beta} - r_{i\alpha}E_{I\beta}^i\right)\right|a\right\rangle. \tag{3.38}$$

Within the CTOCD–DZ scheme the magnetic properties become

$$\chi_{\delta\gamma} = \chi_{\delta\gamma}^{\mathrm{p}} + \chi_{\delta\gamma}^{\Delta}, \qquad \sigma_{\delta\gamma} = \sigma_{\delta\gamma}^{\mathrm{p}I} + \sigma_{\delta\gamma}^{\Delta I}, \tag{3.39}$$

where

$$\chi_{\delta\gamma}^{\Delta} = \frac{e^2}{4m_e^2 c^2\hbar}\epsilon_{\alpha\beta\gamma}\sum_{j\neq a}\omega_{ja}^{-1}\left\{\left\langle a\left|\sum_{i=1}^{n}\left[(r_\beta - r'_\beta)l_\delta\right]_i\right|j\right\rangle\langle j|P_\alpha|a\rangle + \langle a|P_\alpha|j\rangle\left\langle j\left|\sum_{i=1}^{n}\left[(r_\beta - r'_\beta)l_\delta\right]_i\right|a\right\rangle\right\}, \tag{3.40}$$

$$\sigma_{\delta\gamma}^{\Delta I} = -\frac{e^2}{2m_e^2 c^2\hbar}\epsilon_{\alpha\beta\gamma}\sum_{j\neq a}\omega_{ja}^{-1}\left\{\left\langle a\left|\sum_{i=1}^{n}(r_{i\beta} - r'_\beta)m_{I\delta}^i\right|j\right\rangle\langle j|P_\alpha|a\rangle + \langle a\,|P_\alpha|\,j\rangle\left\langle j\left|\sum_{i=1}^{n}(r_{i\beta} - r'_\beta)m_{I\delta}^i\right|a\right\rangle\right\}, \tag{3.41}$$

denoting

$$\mathbf{m}_I^i = |\mathbf{r}_i - \mathbf{R}_I|^{-3}\, \mathbf{l}_i(\mathbf{R}_I) = \frac{1}{e}\mathbf{E}_I^i \times \mathbf{p}_i. \tag{3.42}$$

In approximate calculations adopting the algebraic approximation CTOCD–DZ approach proved to be quite useful: all of the shielding tensor components are independent of origin, and magnetic susceptibility is origin independent in center–symmetric molecules [31–34].

5.3.4 Annihilation of paramagnetic contribution to current density

Another method for calculating magnetic properties has been devised, within the framework of a continuous transformation of origin of current density, formally setting the paramagnetic contribution to zero all over the molecular domain (CTOCD–PZ), see Refs. [34]. To this end, a wider class of transformation functions $\mathbf{d} = \mathbf{d}(\mathbf{r})$ has been introduced [32]. The function killing the paramagnetic current density contribution can be evaluated pointwise via the condition, compare eq. (3.23),

$$\mathbf{J}_p^{\mathbf{B}}(\mathbf{r} - \mathbf{r}') = -\mathbf{J}_p^{\mathbf{d}\times\mathbf{B}}(\mathbf{r}), \tag{3.43}$$

which furnishes the 3×3 system of linear equations

$$\mathbf{M}\mathbf{d} = \mathbf{T}, \tag{3.44}$$

where, compare eq. (3.25),

$$M_{\delta\beta} = \frac{e}{m_e} n \epsilon_{\alpha\beta\gamma} B_\gamma \int d\mathbf{x}_2 \ldots d\mathbf{x}_n \left[\Psi_\alpha^{\mathbf{d}\times\mathbf{B}*} p_\delta \Psi_0 + \Psi_0^* p_\delta \Psi_\alpha^{\mathbf{d}\times\mathbf{B}}\right], \tag{3.45}$$

and

$$T_\delta = -\frac{e}{m_e} n B_\alpha \int d\mathbf{x}_2 \ldots d\mathbf{x}_n \left[\Psi_\alpha^{\mathbf{B}*} p_\delta \Psi_0 + \Psi_0^* p_\delta \Psi_\alpha^{\mathbf{B}}\right]. \tag{3.46}$$

Matrix $\mathbf{M}$ is singular, as it is evident from definition (3.45). This is consistent with the fact that complete annihilation of paramagnetic current is not physically possible; in particular the component parallel to the magnetic field cannot be set to zero, as a diamagnetic contribution is always perpendicular to $\mathbf{B}$. However, one needs to solve, for each point in real space, a 2×2 subsystem of (3.44) to annihilate only the components of the paramagnetic current perpendicular to $\mathbf{B}$; for instance, if $\mathbf{B} \equiv \mathbf{e}_3 B$, only d_x and d_y are to be calculated.

Although the function $\mathbf{d} = \mathbf{d}(\mathbf{r})$ is not known analytically in the case of an approximate wavefunction, its expectation value over that wavefunction can be approximately calculated via eqs. (3.45) and (3.46). Defining the operator

$$D_\alpha = \sum_{i=1}^{n} d_{i\alpha}, \tag{3.47}$$

it is found

$$\int T_\alpha(\mathbf{r})d\mathbf{r} = \frac{e^2 B_\beta}{2m_e^2 c\hbar}\left(P_\alpha, L_\beta\right)_{-1}, \tag{3.48}$$

$$\int M_{\alpha\beta}(\mathbf{r})d_\beta(\mathbf{r})d\mathbf{r} = -\frac{e^2 B_\beta}{2m_e^2 c}\epsilon_{\beta\gamma\delta}\left(P_\gamma, \sum_{i=1}^{n} d_{i\delta}p_{i\alpha}\right)_{-1} = \frac{e^2 B_\beta}{2m_e c}\epsilon_{\alpha\beta\gamma}\left\langle a\left|D_\gamma\right|a\right\rangle, \tag{3.49}$$

so that, owing to eq. (3.44),

$$\int d_\gamma(\mathbf{r})\gamma(\mathbf{r})d\mathbf{r} = \langle a|D_\gamma|a\rangle = \frac{1}{2m_e}\epsilon_{\alpha\beta\gamma}\left(P_\alpha, L_\beta\right)_{-1}. \tag{3.50}$$

As hypervirial relationship (3.14) has been used to write the second of identities (3.49), constraint (3.50) is exactly fulfilled only in the case of exact eigenfunctions to a model Hamiltonian, *e.g.*, in the Hartree–Fock method.

The expectation value of the moments of $\mathbf{d}$ function is also known *a priori*, as it is related to the conventional paramagnetic contribution to susceptibility, *vide infra*.

Within the CTOCD–PZ scheme the current density is completely diamagnetic in form,

$$\mathbf{J}^{\mathbf{B}}(\mathbf{r}) = \mathbf{J}_d^{\mathbf{B}}(\mathbf{r}-\mathbf{r}') + \mathbf{J}_d^{\mathbf{d}\times\mathbf{B}}(\mathbf{r}) =$$

$$-\frac{e^2}{2m_e c}\mathbf{B}\times[\mathbf{r}-\mathbf{d}(\mathbf{r})]\gamma(\mathbf{r}), \tag{3.51}$$

and, from the invariance constraint (3.26) and eq. (3.43),

$$\mathbf{J}_d^{\mathbf{d}\times\mathbf{B}}(\mathbf{r}) = \mathbf{J}_p^{\mathbf{B}}(\mathbf{r}-\mathbf{r}'). \tag{3.52}$$

This relationship (which does not provide a recipe for calculation of the shift functions in the approximate case) yields the definition of exact $\mathbf{d}(\mathbf{r})$,

$$d_\gamma(\mathbf{r}) =$$

$$-n\frac{c}{e}\gamma^{-1}(\mathbf{r})\epsilon_{\alpha\beta\gamma}\int d\mathbf{x}_2\ldots d\mathbf{x}_n\left[\Psi_\beta^{\mathbf{B}*}(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)p_\alpha\Psi_0(\mathbf{r},\mathbf{x}_2,\ldots\mathbf{x}_n) + \Psi_0^*(\mathbf{r},\mathbf{x}_2,\ldots\mathbf{x}_n)p_\alpha\Psi_\beta^{\mathbf{B}}(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)\right], \tag{3.53}$$

so that, consistent with hypervirial condition (3.14), and with eq. (3.50), by integrating (3.53) it is obtained

$$\langle a|D_\gamma|a\rangle = \langle a|R_\gamma|a\rangle. \tag{3.54}$$

This identity is only valid for an exact eigenfunction to a model Hamiltonian, according to constraint (3.12).

Current density tensors within the CTOCD–PZ method can be defined,

$$\mathcal{J}_{p\delta}^{(\mathbf{d}\times\mathbf{B})_\beta}(\mathbf{r}) = -\frac{ne}{m_e}\int d\mathbf{x}_2\ldots d\mathbf{x}_n\left[\Psi_\beta^{(\mathbf{d}\times\mathbf{B})*}(\mathbf{r},\mathbf{x}_2\ldots\mathbf{x}_n)p_\alpha\Psi_0(\mathbf{r},\mathbf{x}_2,\ldots\mathbf{x}_n)\right.$$

$$+\Psi_0^*(\mathbf{r},\mathbf{x}_2,\dots\mathbf{x}_n)p_\alpha\Psi_\beta^{(\mathbf{d}\times\mathbf{B})}(\mathbf{r},\mathbf{x}_2\dots\mathbf{x}_n)\Big], \tag{3.55}$$

$$\mathcal{J}_{d\alpha}^{(\mathbf{d}\times\mathbf{B})_\beta}(\mathbf{r}) = -\frac{e^2}{2m_e c}\delta_{\alpha\beta}\gamma(\mathbf{r}), \tag{3.56}$$

so that

$$J_\alpha^{(\mathbf{d}\times\mathbf{B})} = \left(\mathcal{J}_{d\alpha}^{(\mathbf{d}\times\mathbf{B})_\beta} + \mathcal{J}_{p\alpha}^{(\mathbf{d}\times\mathbf{B})_\beta}\right)\epsilon_{\beta\gamma\delta}d_\gamma B_\delta. \tag{3.57}$$

Allowing for definitions (3.55) and (3.56), "paramagnetic" Π–contributions to magnetic properties can be recast in integral form,

$$\chi_{\alpha\delta}^{\Pi} = \frac{1}{2c}\epsilon_{\alpha\beta\gamma}\epsilon_{\lambda\mu\delta}\int r_\beta\mathcal{J}_{d\gamma}^{(\mathbf{d}\times\mathbf{B})_\lambda}(\mathbf{r})d_\mu(\mathbf{r})d\mathbf{r} = \frac{e^2}{4m_e c^2}\int\gamma(\mathbf{r})\left[d_\beta(\mathbf{r})r_\beta\delta_{\alpha\delta} - d_\alpha(\mathbf{r})r_\delta\right]d\mathbf{r}$$

$$= \frac{e^2}{4m_e c^2}\left\langle a\left|\sum_{i=1}^{n}\left(d_\beta r_\beta\delta_{\alpha\delta} - d_\alpha r_\delta\right)_i\right|a\right\rangle, \tag{3.58}$$

$$\sigma_{\alpha\delta}^{\Pi I} = -\frac{1}{ec}\epsilon_{\alpha\beta\gamma}\epsilon_{\lambda\mu\delta}\int E_{I\beta}(\mathbf{r})\mathcal{J}_{d\gamma}^{(\mathbf{d}\times\mathbf{B})_\lambda}(\mathbf{r})d_\mu(\mathbf{r})d\mathbf{r} = -\frac{e}{2m_e c^2}\int\gamma(\mathbf{r})\left[d_\beta(\mathbf{r})E_{I\beta}(\mathbf{r})\delta_{\alpha\delta} - d_\alpha(\mathbf{r})E_{I\delta}(\mathbf{r})\right]d\mathbf{r}$$

$$= -\frac{e}{2m_e c^2}\left\langle a\left|\sum_{i=1}^{n}\left(d_{i\beta}E_{I\beta}^i\delta_{\alpha\delta} - d_{i\alpha}E_{I\delta}^i\right)_i\right|a\right\rangle, \tag{3.59}$$

where the operator for the electric field exerted by an electron with position $\mathbf{r}$ on nucleus I is denoted by

$$E_{I\beta}(\mathbf{r}) = e\frac{r_\beta - R_{I\beta}}{|\mathbf{r}-\mathbf{R}_I|^3}. \tag{3.60}$$

It can be easily shown that contributions (3.58) and (3.59) reduce to the conventional paramagnetic terms. Using identity (3.53) in the form

$$\epsilon_{\lambda\mu\delta}d_\mu(\mathbf{r})\gamma(\mathbf{r})$$

$$= -\frac{2nc}{e}\int d\mathbf{x}_2\dots d\mathbf{x}_n\left[\Psi_\delta^{B*}(\mathbf{r},\mathbf{x}_2\dots\mathbf{x}_n)p_\lambda\Psi_0(\mathbf{r},\mathbf{x}_2,\dots\mathbf{x}_n) + \Psi_0^*(\mathbf{r},\mathbf{x}_2,\dots\mathbf{x}_n)p_\lambda\Psi_\delta^B(\mathbf{r},\mathbf{x}_2\dots\mathbf{x}_n)\right], \tag{3.61}$$

in eqs. (3.58) and (3.59), the familiar van Vleck [6] and Ramsey [36] terms, compare eqs. (3.35)–(3.38) are recovered,

$$\chi_{\alpha\beta}^{\Pi} = \frac{e^2}{4c^2m_e^2\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\Re\left(\langle a|L_\alpha|j\rangle\langle j|L_\beta|a\rangle\right) = \chi_{\alpha\beta}^{\mathrm{p}}, \tag{3.62}$$

$$\sigma_{\alpha\beta}^{\Pi I} = -\frac{e^2}{2m_e^2c^2\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\Re(\langle a|M_{I\alpha}^n|j\rangle\langle j|L_\beta|a\rangle) = \sigma_{\alpha\beta}^{\mathrm{p}I}. \tag{3.63}$$

Eventually, the physical requirement that $\chi_{\alpha\beta}^{\Pi} = \chi_{\beta\alpha}^{\Pi}$ in definition (3.50) amounts to a "parallelism condition",

$$\epsilon_{\alpha\beta\gamma}\int d_\beta(\mathbf{r})r_\gamma\gamma(\mathbf{r})d\mathbf{r} = 0, \tag{3.64}$$

which can be proven via eq. (3.53).

5.3.5 Gauge translation

It is now interesting to check the dependence of CTOCD–PZ properties on a gauge translation (3.19). Assuming the origin shift $\mathbf{v} = \mathbf{r}'' - \mathbf{r}'$, we find

$$\chi^{\mathrm{d}}_{\alpha\beta}(\mathbf{r}^{''})$$

$$= \chi^{\mathrm{d}}_{\alpha\beta}(\mathbf{r}^{'}) + \frac{e^2}{4m_e c^2}\left\{\delta_{\alpha\beta}\left[2v_\gamma \langle a|R_\gamma|a\rangle - nv_\gamma v_\gamma\right] - v_\alpha \langle a|R_\beta|a\rangle - v_\beta \langle a|R_\alpha|a\rangle + nv_\alpha v_\beta\right\}, \tag{3.65}$$

$$\chi^{\Pi}_{\alpha\beta}(\mathbf{r}'') =$$

$$\chi^{\Pi}_{\alpha\beta}(\mathbf{r}') - \frac{e^2}{4m_e c^2}\left\{\delta_{\alpha\beta}\left[v_\gamma\left(\langle a\,|R_\gamma|\,a\rangle + \langle a\,|D_\gamma|\,a\rangle\right) - nv_\gamma v_\gamma\right] . - v_\alpha \langle a\,|R_\beta|\,a\rangle - v_\beta \langle a\,|D_\alpha|\,a\rangle + nv_\alpha v_\beta\right\}, \tag{3.66}$$

Comparing eqs. (3.65) and (3.66) for magnetizability, one can notice the exact cancellation of the quadratic term in $\mathbf{v}$. Therefore, theoretical components of total CTOCD–PZ magnetizability tensor depend only linearly on the change of origin. The constraint for invariance of magnetic susceptibility to a gauge traslation is provided by identity (3.54), which is also consistent with the integral condition for charge–current conservation,

$$\int J^{\mathbf{B}}_{\alpha} d\mathbf{r} = \int J^{\mathbf{B}}_{d\alpha} d\mathbf{r} + \int J^{\mathbf{d}\times\mathbf{B}}_{d\alpha} d\mathbf{r} = 0. \tag{3.67}$$

These equations indicate that total CTOCD–PZ magnetic susceptibility is invariant to a gauge translation in the case of center–symmetric molecule, where $\langle a|\mathbf{R}|a\rangle = \langle a|\mathbf{D}|a\rangle = \mathbf{0}$. At any rate, even if these expectation values are calculated over approximate wavefunctions, their difference is generally expected to be rather small. In other words, CTOCD–PZ magnetic susceptibilities are characterized by a fairly good degree of origin independence also within the algebraic approximation, using basis sets of small size.

Interestingly enough, total components of the shielding tensors evaluated within the CTOCD–PZ method are independent of gauge translation, as in the CTOCD–DZ scheme, irrespective of the approximations adopted to evaluate electronic wavefunctions, as there is exact cancellation between "paramagnetic" Π–contributions and ordinary d–contributions, according to formulae

$$\sigma^{\mathrm{d}I}_{\alpha\beta}(\mathbf{r}^{''}) = \sigma^{\mathrm{d}I}_{\alpha\beta}(\mathbf{r}^{'}) - \frac{e}{2m_e c^2}(v_\gamma \left\langle a|E^n_{I\gamma}|a\right\rangle \delta_{\alpha\beta} - v_\alpha \left\langle a|E^n_{I\beta}|a\right\rangle), \tag{3.68}$$

$$\sigma^{\Pi I}_{\alpha\beta}(\mathbf{r}'') = \sigma^{\Pi I}_{\alpha\beta}(\mathbf{r}') + \frac{e}{2m_e c^2}(v_\gamma \langle a|E^n_{I\gamma}|a\rangle \delta_{\alpha\beta} - v_\alpha \langle a|E^n_{I\beta}|a\rangle). \tag{3.69}$$

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